

**Remarks**

Claims 12, 69, and 72 have been amended. Claims 1-80 are pending.

Examination and reconsideration of the application as amended is requested.

Support for the amendment to claim 12 can be found in the specification, for example, on page 9, lines 27-31, bridging sentence, page 10, lines 1-7.

Claims 69 and 73 have been amended to correct obvious grammatical errors. It is submitted that these amendments to claims 69 and 72 are not narrowing amendments.

**New Matter Rejection**

The amendment to page 41, lines 21-22, filed December 28, 2000, is said to introduce new matter. It is required that this "new matter" be canceled. The amendment in question has been amended to provide the original, as-filed, text. The amendment was based on the scanning electron photomicrograph in originally filed FIG. 9. Hence, even through page 41, lines 21-22 has been amended to provide the original text, the scanning electron photomicrograph speaks for itself.

**§ 112 Rejections**

Claims 1-80 stand rejected under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which Applicant regards as the invention.

Claims 1 and 29 are said to be indefinite as to the phrase "volume of said particle, eutectic material" because it is alleged that the phrase appears to be incomplete. It is suggested in the Office Action that "volume of said particle, eutectic material" be changed to "volume of said particle, of a eutectic material".

It is submitted that the as-filed language is not indefinite. That is, the as-filed language is clear the suggested insertion of "of a" is not needed.

BEST AVAILABLE COPY

Claims 7, 8, 20, 26, and 32 are said to be indefinite as to the phrase “are, on average up to” as it is alleged it is unclear as to what it encompasses. It is suggested that “on average” be canceled.

As discussed at the October 16, 2001 interview, it is submitted that the as-filed language is clear. For example, in claim 10 it means the average size of the colonies is up to 10 micrometers (i.e., the average size of the colonies is not greater than 10 micrometers).

Claim 12 is said to be indefinite because it is alleged that it is unclear what “cations” encompasses.

Claim 12 has been amended as discussed at the October 16, 2001 interview.

Claim 13 is said to be indefinite because it is alleged that the phrase “a portion of said complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  Al cations are substituted” is not defined in a clear and concise manner. One suggestion in the Office Action is to amend the claim to reflect that “wherein in a portion of the Al cations in the complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  (sic) are substituted ...”.

As discussed at the October 16, 2001 interview, the as-filed claim has the same meaning as the latter suggestion. Hence, it is submitted that amendment is not necessary.

Claims 14 and 15 are said to be indefinite because it is alleged that the phrase “a portion of said complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  Y cations are substituted” is not defined in a clear and concise manner. One suggestion in the Office Action is to amend the claim to reflect that “wherein in a portion of the Y cations in the complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  (sic) are substituted ...”.

As discussed at the October 16, 2001 interview, the as-filed claim has the same meaning as the latter suggestion. Hence, it is submitted that amendment is not necessary.

Claims 36, 39, 41, 44, 46, 52, 53, 59, 61, 67, 69, and 72 are said to be indefinite as to the phrase “volume of the respective particle, eutectic material” because it is alleged that the phrase appears to be incomplete. It is suggested in the Office Action that “volume of the respective particle, eutectic material” be changed to “volume of the respective particle, of a eutectic material”.

It is submitted that the as-filed language is not indefinite. That is, the as-filed language is clear the suggested insertion of “of a” is not needed.

Claims 41 and 44 are said to be indefinite as to the phrase "specified nominal grade" because it is alleged that it is unclear as to what it encompasses, rendering the claims unclear.

As discussed at the October 16, 2001 interview, the phrase "specified nominal grade" refers to industry accepted grading standards such as those known as the American National Standards Institute, Inc. (ANSI) standards, Federation of European Producers of Abrasive Products (FEPA) standards, and Japanese Industrial Standard (JIS) standards (see, e.g., page 20, lines 21-31, bridging paragraph, page 21, lines 1-6).

Claims 46 and 52 are said to be indefinite because it is alleged that "the converting step" is unclear.

As discussed at the October 16, 2001 interview, the meaning of "the converting step" is clear after reviewing, for example, page 18, line 10 to page 20, line 3.

In summary, Applicant submits the rejection of claims 1-80 under 35 U.S.C. § 112, second paragraph, should be withdrawn.

### **§103 Rejections**

Claims 1-12, 16-34, 36-39, 41-44, 46-52, and 75-80 stand rejected under 35 U.S.C. §103 as being unpatentable over EP 480,678. Claims 53-59, 61-67, and 69-74 stand rejected under 35 U.S.C. §103 as being unpatentable over EP 480,678 in view of U.S. Pat. No. 4,035,162 (Brothers et al.). Claims 1-9, 11, 16-20, 22-26, 28-32, 34-60, and 69-80 stand rejected under 35 U.S.C. §103 as being unpatentable over U.S. Pat. No. 4,457,767 (Poon et al.). Claims 61-68 stand rejected under 35 U.S.C. §103 as being unpatentable over '767 (Poon et al.) in view of '162 (Brothers et al.). Claims 1-4, 9-12, 16-19, 21-25, 27-31, 33-52, and 75-80 stand rejected under 35 U.S.C. §103 as being unpatentable over U.S. Pat. No. 5,981,415 (Waku et al.). Claims 53-74 stand rejected under 35 U.S.C. §103 as being unpatentable over '415 (Waku et al.) in view of '162 (Brothers et al.). Claims 1-12, 16-52, and 75-80 stand rejected under 35 U.S.C. §103 as being unpatentable over U.S. Pat. No. 4,595,663 (Krohn et al.) alone or in view of '415 (Waku et al.). Claims 53-74 stand rejected under 35 U.S.C. §103 as being unpatentable over '663 (Krohn et al.) in view of '415 (Waku et al.) and further in view of '162 (Brothers et al.).

The rejections of claims 1-12, 16-34, 36-39, 41-44, 46-52, and 75-80 under 35 U.S.C. §103 as being unpatentable over EP 480,678, claims 53-59, 61-67, and 69-74 over EP 480,678 in view of '162 (Brothers et al.), claims 1-9, 11, 16-20, 22-26, 28-32, 34-60, and 69-80 over '767 (Poon et al.), claims 61-68 over '767 (Poon et al.) in view of '162 (Brothers et al.), claims 1-4, 9-12, 16-19, 21-25, 27-31, 33-52, and 75-80 over '415 (Waku et al.), claims 53-74 over '415 (Waku et al.) in view of '162 (Brothers et al.), claims 1-12, 16-52, and 75-80 over '663 (Krohn et al.) alone or in view of '415 (Waku et al.), claims 53-74 over '663 (Krohn et al.) in view of '415 (Waku et al.) and further in view of '162 (Brothers et al.), should be withdrawn.

Each of Applicant's independent claims 1 (which is directed toward a fused, crystalline abrasive particle), 36 (which is directed toward a plurality of particles), 41 (which is directed toward a plurality of abrasive particles having a specified nominal grade), 46 (which is directed toward a method for making fused, crystalline abrasive particles), 53 (which is directed toward an abrasive article), 61 (which is directed toward a vitrified bonded abrasive article), and 69 (which is directed toward a method of abrading a surface) require eutectic of at least:

(a) crystalline ZrO<sub>2</sub> and

(b) at least two of:

(i) crystalline Al<sub>2</sub>O<sub>3</sub>,

(ii) first crystalline complex Al<sub>2</sub>O<sub>3</sub>·Y<sub>2</sub>O<sub>3</sub>, or

(iii) second, different, crystalline complex Al<sub>2</sub>O<sub>3</sub>·Y<sub>2</sub>O<sub>3</sub>.

It is submitted that none of the references relied upon in the §103 rejections (teach or) properly suggest, for example, such eutectic.

As discussed at the October 16, 2001 interview, in response to the Examiner asking if yttria, Y<sub>2</sub>O<sub>3</sub>, is a rare earth oxide, it was stated that Y<sub>2</sub>O<sub>3</sub>, is not a rare earth oxide. Applicant has clearly defined the term rare earth oxides (or REO) on page 5, lines 12-14 as, on a theoretical oxide basis, CeO<sub>2</sub>, Dy<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Sm<sub>2</sub>O<sub>3</sub>, Th<sub>4</sub>O<sub>7</sub>, Tm<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub>. Further, it was stated the open-ended language of Applicant's claims permits the inclusion of rare earth oxide in addition to the required Y<sub>2</sub>O<sub>3</sub>.

Further, each of Applicant's independent claims 29 (which is directed toward a fused, crystalline abrasive particle), 39 (which is directed toward a plurality of particles), 44 (which is directed toward a plurality of abrasive particles having a specified nominal grade), 52

(which is directed toward a method for making fused, crystalline abrasive particles), 59 (which is directed toward an abrasive article), 67 (which is directed toward a vitrified bonded abrasive article), and 72 (which is directed toward a method of abrading a surface) require eutectic of at least: (a) crystalline complex Al<sub>2</sub>O<sub>3</sub>·Y<sub>2</sub>O<sub>3</sub> and (b) crystalline ZrO<sub>2</sub>. It is submitted that none of the references relied upon in the §103 rejections (teach or) properly suggest, for example, such eutectic.

Before distinguishing the references relied upon for the §103 rejections, it is submitted that it is well known in the ceramic art that when processing two oxides (say, oxide-A and oxide-B), for example, to provide a ceramic material, the resulting material may not necessarily be a phase of oxide-A and a phase of oxide-B. Depending, for example, on the particular oxides, the initial form of the oxides, the processing, and/or other materials present, the resulting material may be crystalline, glass, or both. Crystalline material may be, for example, one or more phases of oxide-A; one or more phases of oxide-B; a reaction product of oxide-AB; if other oxides are present, a reaction product of oxide-A and/or oxide-B and other oxide; a solid solution of oxide-A and oxide-B, if other oxides are present, a solid solution of oxide-A and/or oxide-B and another oxide, or combinations thereof. Further, for example, the crystals or phases may be in any of a variety of morphologies.

With regard to ZrO<sub>2</sub>, which is one of the oxides that must be present in Applicant's required eutectic, it is well known in the art that additives such as MgO, CaO, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and other rare-earth oxides, are commonly used to stabilize ZrO<sub>2</sub>, in the tetragonal and/or cubic phase (see, e.g., pages 2-5 and 41-47 of Transformation Toughening of Ceramics; D.J Green et al., CRC Press, 1989 (copy enclosed)). As discussed in Transformation Toughening of Ceramics, MgO, CaO, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and other rare-earth oxides in the amounts commonly used for stabilizing the ZrO<sub>2</sub>, form a solid solution with the ZrO<sub>2</sub>.

#### EP 480,678

EP 480,678 reports alumina-zirconia abrasives, which optionally include at least one oxide selected from the group consisting of yttrium oxide, calcium oxide, magnesium oxide, titanium oxide, and other rare earth oxides **in the form of solid solutions** with ZrO<sub>2</sub>. Further, for example, on page 3, lines 43-45, the role of the optional additives as stabilizing oxides is discussed. Clearly, '678 is directed toward the use of yttrium oxide, calcium oxide, magnesium oxide, titanium oxide, and other rare earth oxides to stabilize ZrO<sub>2</sub>, and such oxides form **solid solutions** with ZrO<sub>2</sub>, and does not teach or properly suggest even a

crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , let alone a eutectic as required in each of Applicant's independent claims.

**EP 480,678 in view of U.S. Pat. No. 4,035,162 (Brothers et al.)**

U.S. Pat. No. 4,035,162 (Brothers et al.) is relied upon to show that alumina/zirconia fused abrasive grains are known to be used as abrasives in the manufacture of bonded abrasives (vitrified bond) and coated abrasives.

The independent claims rejected based on '678 in view '162 (Brothers et al.) include, for example, the limitations of claim 1 plus additional limitations. Claim 1 is patentable over '678, for example, for the reasons given above. While not agreeing that there is even proper motivation to combine '678 and '162, even if combined the result is not Applicant's claimed invention as '162 fails to overcome the deficiencies of '678 discussed above.

**U.S. Pat. No. 4,457,767 (Poon et al.)**

U.S. Pat. No. 4,457,767 (Poon et al.) reports 0.1-2 wt.% additions of  $\text{Y}_2\text{O}_3$  to co-fused alumina-zirconia. Referring to an article entitled "Solidus Surface and Phase Equilibria During The Solidification Of Alloys In The  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$  System" by S. N. Lakiza et al., Powder Metallurgy and Metal Ceramics, Vol. 34, Nos. 1-2, 1995 (copy enclosed), it is submitted that for the compositions referred to in '767, the  $\text{Y}_2\text{O}_3$  will be in the form of a **solid solution** with  $\text{ZrO}_2$ . Hence, '767 does not teach or properly suggest even a crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , let alone a eutectic as required in each of Applicant's independent claims.

**U.S. Pat. No. 4,457,767 (Poon et al.) in view of U.S. Pat. No. 4,035,162 (Brothers et al.)**

'162 (Brothers et al.) is relied upon to show that fused abrasive grains are known to be used as abrasives in the manufacture of vitrified bonded abrasives.

The independent claims rejected based on '767 (Poon et al.) in view '162 (Brothers et al.) include, for example, the limitations of claim 1 plus additional limitations. Claim 1 is patentable over '767, for example, for the reasons given above. While not agreeing that there is even proper motivation to combine '767 and '162, even if combined the result is not Applicant's claimed invention as '162 fails to overcome the deficiencies of '767 discussed above.

**U.S. Pat. No. 5,981,415 (Waku et al.)**

U.S. Pat. No. 5,981,415 (Waku et al.) reports a ceramic composite material consisting of two or more crystal phases of different components, each crystal phase having non-regular shape, the shape crystal phases having three dimensional continuous structures intertwined with other, at least one crystal phase thereof being a single crystal. The two or more crystal phases of different components constituting the ceramic material may be those of a combination of a eutectic system. It is said the metal oxides include aluminum oxide ( $\text{Al}_2\text{O}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ), magnesium oxide ( $\text{MgO}$ ), silicon oxide ( $\text{SiO}_2$ ), titanium oxide ( $\text{TiO}_2$ ), barium oxide ( $\text{BaO}$ ), beryllium oxide ( $\text{BeO}$ ), calcium oxide ( $\text{CaO}$ ), chromium oxide ( $\text{Cr}_2\text{O}_3$ ), and rare earth oxides such as  $\text{La}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Tb}_4\text{O}_7$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Tm}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and  $\text{Lu}_2\text{O}_3$ . The complex oxides are said to include  $\text{LaAlO}_3$ ,  $\text{CeAlO}_3$ ,  $\text{PrAlO}_3$ ,  $\text{NdAlO}_3$ ,  $\text{SmAlO}_3$ ,  $\text{EuAlO}_3$ ,  $\text{GdAlO}_3$ ,  $\text{DyAlO}_3$ ,  $\text{ErAlO}_3$ ,  $\text{Yb}_4\text{AlO}_9$ ,  $\text{Er}_3\text{Al}_5\text{O}_{12}$ ,  $11\text{Al}_2\text{O}_3\cdot\text{La}_2\text{O}_3$ ,  $11\text{Al}_2\text{O}_3\cdot\text{Nd}_2\text{O}_3$ ,  $3\text{Dy}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ ,  $2\text{Dy}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ ,  $11\text{Al}_2\text{O}_3\cdot\text{Pr}_2\text{O}_3$ ,  $\text{EuAl}_{11}\text{O}_{18}$ ,  $2\text{Gd}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ ,  $11\text{Al}_2\text{O}_3\cdot\text{Sm}_2\text{O}_3$ ,  $\text{Yb}_3\text{Al}_5\text{O}_3$ ,  $\text{CeAl}_{11}\text{O}_{18}$ , and  $\text{Er}_2\text{Al}_2\text{O}_9$ .

Notwithstanding the eutectics reported in '415 (Waku et al.), there is no teaching or proper suggestion therein of the at least ternary eutectic as required in Applicant's independent claims 1, 36, 41, and 46, or at least the specific binary eutectic (i.e., eutectic of at least crystalline complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  and (b) crystalline  $\text{ZrO}_2$ ) as required in Applicant's independent claims 29, 39, 44, and 52. For example, for Applicant's claims 1, 36, 41, and 46, even if '415 taught or suggested making a material comprising crystalline  $\text{ZrO}_2$  and (b) at least two of (i) crystalline  $\text{Al}_2\text{O}_3$ , (ii) first crystalline complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , or (iii) second, different, crystalline complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , it is not clear the result would be eutectic of such oxides as required by Applicant. Similarly, for Applicant's claims 29, 39, 44, and 52, even if '415 taught or suggested making a material comprising crystalline complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  and crystalline  $\text{ZrO}_2$ ), it is not clear the result would be eutectic of such oxides as required by Applicant.

Although not necessary to overcome the rejection of '415 (Waku et al.), it is submitted that there is no teaching or proper suggestion of an abrasive particle(s) as required by Applicant. Notwithstanding that reference is made to "abrasives" in a portion of the "Background" section (see col. 2, line 54), and that it is stated that "ceramic composite material of the present invention may be useful in many applications in which oxide ceramics such as  $\text{Al}_2\text{O}_3$  are in practice used", and cutting tool members is listed (see col. 9, line 3) as

such an application, '415 does not teach or properly suggest abrasive particle(s). It is submitted that to reach the conclusion that '415 teaches or suggests that the '415 material is useful in the form of abrasive particles requires an impermissible, strained reading of '415 that effectively includes the improper use of hindsight analysis.

**U.S. Pat. No. 5,981,415 (Waku et al.) in view of U.S. Pat. No. 4,035,162 (Brothers et al.)**

'162 (Brothers et al.) is relied upon to show that fused abrasive grains are known to be used as abrasives in the manufacture of bonded abrasives and coated abrasives.

The independent claims rejected based on '415 (Waku et al.) in view '162 (Brothers et al.) include, for example, the limitations of claim 1 plus additional limitations. Claim 1 is patentable over '415, for example, for the reasons given above. While not agreeing that there is even proper motivation to combine '415 and '162, even if combined the result is not Applicant's claimed invention as '162 fails to overcome the deficiencies of '415 discussed above.

**U.S. Pat. No. 4,595,663 (Krohn et al.)**

U.S. Pat. No. 4,595,663 (Krohn et al.) reports ceramic articles containing eutectic constituents consisting of zirconium oxide, hafnium oxide, and mixtures thereof. '663 also reports ceramic articles consisting wholly or predominately of a eutectic constituent of aluminum oxide, zirconium oxide and/or hafnium oxide, which in addition contains yttrium oxide, magnesium oxide, and/or ytterbium oxide. Working Example 1 consists of 57% by weight  $\text{Al}_2\text{O}_3$ , 38% by weight  $\text{ZrO}_2$ , and 5% by weight  $\text{Yb}_2\text{O}_3$  (a rare earth oxide). Further, working Example 5 consists of 50% by weight  $\text{Al}_2\text{O}_3$ , 25 % by weight  $\text{ZrO}_2$ , and 25 % by weight  $\text{Y}_2\text{O}_3$ , working Example 6, 49% by weight  $\text{Al}_2\text{O}_3$ , 28% by weight  $\text{ZrO}_2$ , and 23% by weight  $\text{Y}_2\text{O}_3$ .

Contrary to the assertion in the Office Action that Applicant is claiming a "material", Applicant submits that the "fused, crystalline abrasive(s)" language in the claims is a claim limitation.

There is no teaching or proper suggestion, for example, in '663 (Krohn et al.) of an abrasive particle(s), which is required in each of Applicant's independent claims.

**U.S. Pat. No. 4,595,663 (Krohn et al.) in view of U.S. Pat. No. 5,981,415 (Waku et al.)**

As discussed above, '415 (Waku et al.) does not teach or properly suggest abrasive particles. Hence in addition to the other deficiencies of '663 (Krohn et al.) and '415, and assuming arguendo there is proper motivation to combine '663 and '415, there would still remain an absence of a teaching or proper suggestion of an abrasive particle(s).

**U.S. Pat. No. 4,595,663 (Krohn et al.) in view of U.S. Pat. No. 5,981,415 (Waku et al.), and further in view of .U.S. Pat. No. 4,035,162 (Brothers et al.)**

'162 (Brothers et al.) is relied upon to show that fused abrasive grains are known to be used as abrasives in the manufacture of bonded abrasives and coated abrasives

The independent claims rejected based on to '663 (Krohn et al.) in view of '415 (Waku et al.), and further in view of '162 (Brothers et al.) include, for example, the limitations of claim 1 plus additional limitations. Claim 1 is patentable over '663 in view of '415, for example, for the reasons given above. While not agreeing that there is even proper motivation to combine '663, '415, and '162, even if combined the result is not Applicant's claimed invention as '162 fails to overcome the deficiencies of '663 and '415 discussed above.

Claims 2-28 add additional limitations to claim 1. Claim 1 is patentable for the reasons given above. Thus, claims 2-28 should also be patentable.

Claims 30-35 add additional limitations to claim 29. Claim 1 is patentable for the reasons given above. Thus, claims 30-35 should also be patentable.

Claims 37 and 38 add additional limitations to claim 36. Claim 1 is patentable for the reasons given above. Thus, claims 37 and 38 should also be patentable.

Claim 40 adds an additional limitation to claim 39. Claim 39 is patentable for the reasons given above. Thus, claim 40 should also be patentable.

Claims 42, 43, and 75-77 add additional limitations to claim 41. Claim 41 is patentable for the reasons given above. Thus, claims 42, 43, and 75-77 should also be patentable.

Claims 45 and 78-80 add additional limitations to claim 44. Claim 44 is patentable for the reasons given above. Thus, claims 45 and 78-80 should also be patentable.

Claims 47-51 add additional limitations to claim 1. Claim 46 is patentable for the reasons given above. Thus, claims 47-51 should also be patentable.

Claims 54-58 add additional limitations to claim 53. Claim 53 is patentable for the reasons given above. Thus, claims 54-58 should also be patentable.

Claim 60 adds an additional limitation to claim 59. Claim 59 is patentable for the reasons given above. Thus, claim 60 should also be patentable.

Claims 62-66 add additional limitations to claim 61. Claim 61 is patentable for the reasons given above. Thus, claims 62-66 should also be patentable.

Claim 68 adds an additional limitation to claim 67. Claim 67 is patentable for the reasons given above. Thus, claim 68 should also be patentable.

Claims 70 and 71 add additional limitations to claim 69. Claim 69 is patentable for the reasons given above. Thus, claims 70 and 71 should also be patentable.

Claims 73 and 74 add additional limitations to claim 72. Claim 72 is patentable for the reasons given above. Thus, claims 73 and 74 should also be patentable.

In summary, the rejections of claims 1-12, 16-34, 36-39, 41-44, 46-52, and 75-80 under 35 U.S.C. §103 as being unpatentable over EP 480,678, claims 53-59, 61-67, and 69-74 over EP 480,678 in view of '162 (Brothers et al.), claims 1-9, 11, 16-20, 22-26, 28-32, 34-60, and 69-80 over '767 (Poon et al.), claims 61-68 over '767 (Poon et al.) in view of '162 (Brothers et al.), claims 1-4, 9-12, 16-19, 21-25, 27-31, 33-52, and 75-80 over '415 (Waku et al.), claims 53-74 over '415 (Waku et al.) in view of '162 (Brothers et al.), claims 1-12, 16-52, and 75-80 over '663 (Krohn et al.) alone or in view of '415 (Waku et al.), and claims 53-74 over '663 (Krohn et al.) in view of '415 (Waku et al.) and further in view of '162 (Brothers et al.), should be withdrawn.

### **Double Patenting Rejections**

Claims 1-80 are provisionally rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over all the claims of applications having U.S. Serial Nos. 09/772,730, 09/618,879, 09/619,106, 09/619,289, 09/704,843, 09/619,215, 09/619,729, 09/620,262, and 09/619,192. In view of these obviousness-type double patenting rejections, the undersigned again brought to the Examiner's attention applications having U.S. Serial Nos. 09/619,191, 09/619,563, and 09/619,744 (cited in the Information Disclosure Statement bearing a certificate of mailing date of November 6, 2000).

While not agreeing that these rejections are correct (or one based on applications having U.S. Serial Nos. 09/619,191, 09/619,563, and 09/619,744), to facilitate prosecution,

enclosed is a terminal disclaimer which obviates this rejection is being submitted with this response.

**Interview Summary**

The undersigned acknowledges with appreciation the in person interview granted by the Examiner on October 16, 2001, the essence of which is described herein.

In view of the above, it is submitted that the application is in condition for allowance. Reconsideration of the rejection is requested. Allowance of claims 1-80, as amended, at an early date is solicited.

Registration Number 35,048	Telephone Number 651-736-0641
Date <i>December 19, 2001</i>	

Respectfully submitted,

By

  
Gregory D. Allen

Office of Intellectual Property Counsel  
3M Innovative Properties Company  
P.O. Box 33427  
St. Paul, Minnesota 55133-3427  
Facsimile: (651) 736-3833

p:\allengre\appn\55000\55763\55763-a\55763.002.rsl.doc

**Version With Markings to Show Changes Made****In The Specification**

On page 41, please amend the following paragraph starting on line 13 and ending on line 22:

FIG. 9 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Comparative Example A) of fused Comparative Example E material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies are about 10-40 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example E material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions a crystalline  $\text{Al}_2\text{O}_3$ -rich spinel solid solution phase. The width of these phases observed in the polished section were up to about 2[1] micrometers.

**In The Claims**

Please amend claims 12, 69, and 72 as follows:

12. The fused, crystalline abrasive particle according to claim 3, wherein said complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$  further comprises cations selected from the group consisting of Cr, Ti, Sc, Fe, Mg, Ca, Si, Co, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Th, Tm, Yb, and combinations thereof [in addition to Al and Y].

69. A method of abrading a surface, said method comprising:  
contacting at least one fused, crystalline abrasive particle comprising at least 20 percent by volume, based on the total volume of the respective particle, eutectic material, wherein said eutectic material comprises eutectic of at least (a) crystalline  $\text{ZrO}_2$  and (b) at least two of (i) crystalline  $\text{Al}_2\text{O}_3$ , (ii) first crystalline complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , or (iii) second, different, crystalline complex  $\text{Al}_2\text{O}_3\cdot\text{Y}_2\text{O}_3$ , with a surface of a workpiece; and  
moving at least one of [one]said fused abrasive particle or said surface relative to the other to abrade at least a portion of said surface with said fused abrasive particle.

72. A method of abrading a surface, said method comprising:  
contacting at least one fused, crystalline abrasive particle comprising at  
least 20 percent by volume, based on the total volume of the respective particle, eutectic  
material, wherein said eutectic material comprises eutectic of at least (a) crystalline complex  
 $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  and (b) crystalline  $\text{ZrO}_2$ , with a surface of a workpiece; and  
moving at least one of [one] said fused abrasive particle or said surface  
relative to the other to abrade at least a portion of said surface with said fused abrasive  
particle.



# Transformation Toughening of Ceramics

## Authors

**D. J. Green, Ph.D.**

Department of Materials Science and Engineering  
The Pennsylvania State University  
University Park, Pennsylvania

**R. H. J. Hannink, Ph.D., and M. V. Swain, Ph.D.**

Division of Materials Science and Technology  
Commonwealth Scientific and Industrial Research Organization  
Clayton, Victoria, Australia

RECEIVED  
FEB 04 2002  
TC-170



CRC Press, Inc.  
Boca Raton, Florida



**Library of Congress Cataloging-in-Publication Data**

Green, D. J.

Transformation toughening of ceramics.

Bibliography: p.

Includes index.

1. Ceramic materials—Mechanical properties.

I. Hannink, R. H. J. II. Swain, M. V. III. Title.

TA455.C43G74 1989 666 88-25805

ISBN 0-8493-6594-5

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

© 1989 by CRC Press, Inc.

International Standard Book 0-8493-6594-5

Library of Congress Card Number 88-25805  
Printed in the United States

perspective and a materials science viewpoint. This latter approach stresses the relationship between the structure of a material, i.e., atomic, electronic, microscopic, etc., the properties of a material, and the fabrication procedure that is used to produce a specific structure. The interplay between these elements represents a basic philosophy in materials science. There have been previous and extensive reviews on the science and technology of zirconia and these should be consulted for further details.<sup>3-6</sup>

### III. HISTORICAL PERSPECTIVE

$\text{ZrO}_2$  was discovered in Brazil as the naturally occurring mineral, baddeleyite, by Hussak in 1892.<sup>3</sup> This rich mineral usually contains about 80%  $\text{ZrO}_2$ , but it can be as high as 90%.<sup>3</sup> The major impurities in this mineral are usually  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , etc. The other main source of  $\text{ZrO}_2$  is zircon ( $\text{ZrSiO}_4$ ), which occurs as secondary deposits in India, Australia, and the U.S.  $\text{ZrO}_2$  is not a rare substance and represents about 0.02 to 0.03% of the Earth's crust. It is, however, often found in small concentrations. For example,  $\text{ZrSiO}_4$  is found in igneous rocks and crystalline schists and the crystals possess a high refractive index and are often prized as gems. Zircon crystals can be water clear, somewhat like diamonds, or can display vivid colors such as the topaz-colored hyacinth stones of Sri Lanka. Thus, although  $\text{ZrO}_2$  is relatively abundant, rich  $\text{ZrO}_2$ -yielding ores are relatively scarce, but less so than many metallic ores, such as tin or copper.

Zr belongs in the fourth group of the Periodic Table, between Ti and Hf. The chemistry and crystal structures of  $\text{HfO}_2$  and  $\text{ZrO}_2$  are very similar. Moreover,  $\text{HfO}_2$  is often found in  $\text{ZrO}_2$  ores with the amount varying from 2 to 22%. The first industrial use of  $\text{ZrO}_2$  was as a refractory material by Germany in World War I, but as we shall see, there are many unusual properties of this material in addition to its refractoriness.

Pure  $\text{ZrO}_2$  exists in three different crystal structures, i.e., monoclinic, tetragonal, and cubic. The monoclinic crystal structure was identified by Ruff and Ebert<sup>7</sup> using X-ray diffraction. In addition, they found that the monoclinic form undergoes a disruptive phase transformation to the tetragonal form  $\sim 1100^\circ\text{C}$ . The phase transformation usually leads to the shattering of a body, but it was found that  $\text{ZrO}_2$  could form a fluorite-type cubic phase by the addition of various metal oxides.<sup>8,9</sup> This process removes the disruptive transformation and stabilizes the cubic phase at low temperatures and, hence, such materials were called (cubic) stabilized zirconias (CSZ).

The alloying oxides used to stabilize the cubic phase act to lower the phase transformation temperatures as they are added to the  $\text{ZrO}_2$ . Thus, it is possible to produce materials which are a mixture of the cubic and monoclinic (or tetragonal) phases. These materials are called partially stabilized zirconias (PSZ) and were found to be useful because they possess better thermal shock resistance than CSZ. The equilibrium stability regions of phases are generally shown in phase diagrams. Figure 1 shows an example of possible zirconia-metal oxide diagram in which the solid solution cubic phase is formed. In this diagram, the monoclinic/tetragonal transformation in pure zirconia is shown to occur at  $1200^\circ\text{C}$ . As we add metal oxide, we find solid solution regions for the tetragonal and monoclinic phases and the transformation temperature decreases to  $<600^\circ\text{C}$  at the eutectoid composition of  $\sim 4.8$  mol% metal oxide. For larger metal oxide additions, the solid solution cubic phase appears, in which the cubic phase is stable down to room temperature. The single phase, solid solution regions are separated by various two-phase regions, i.e., cubic + tetragonal, cubic + monoclinic, and tetragonal + monoclinic. The phase diagrams of the binary oxide systems that form CSZ and PSZ have been reviewed by Stubican and Hellmann.<sup>10</sup>

The tetragonal-monoclinic phase transformation in  $\text{ZrO}_2$  has been the subject of considerable study. Wolten<sup>11</sup> was the first to suggest that the transformation was martensitic, i.e., similar to that of martensite, which is used to harden steels by specific heat treatments.

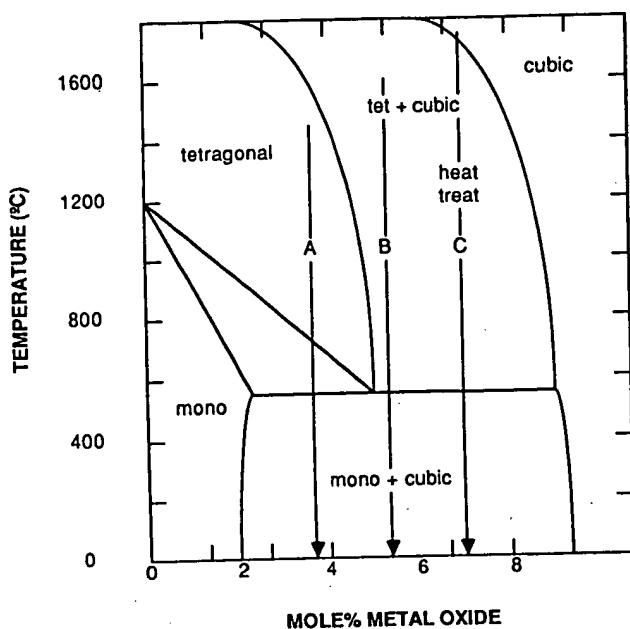


FIGURE 1. A schematic metal oxide-zirconia phase diagram showing routes for fabricating three different microstructures.

Similarly, it was the studies of the  $\text{ZrO}_2$  phase transformation and how it could be controlled by heat treatments in PSZ, that led to the discovery of transformation toughening.<sup>12</sup>

As discussed above, it had been found that the PSZ materials often had superior mechanical properties compared to the CSZ materials, particularly their thermal shock resistance. This led to a variety of scientific studies that were aimed at understanding the mechanical behavior of PSZ. It was clear that the lower values of the thermal expansion coefficients compared to CSZ were part of the answer, but the attention turned to the microstructure of the PSZ materials in order to understand the effect of the tetragonal to monoclinic phase transformation on the mechanical properties. King and Yavorsky<sup>13</sup> argued that the stresses that accompany the transformation led to plastic deformation of the cubic grains and this form of stress relief reduced the possibility of failure. In a later study by Garvie and Nicholson,<sup>14</sup> it was suggested that microcracking, rather than plastic deformation, was the cause of the superior thermal shock resistance, that is, the stresses produced by the phase transformation were relieved by the formation of microscopic cracks. These microcracks were associated with the local stress field of the transforming particles and, hence, could be arrested. It was then suggested using a concept put forward by Hasselman,<sup>15</sup> that such microcracks would propagate quasi-statically in response to thermal stresses. In other words, if there is a sufficient density of microcracks, they propagate in a stable fashion so that rather than a sudden reduction in strength, thermal shock would lead to only a gradual reduction in strength.

At this point, it was realized that the microstructure of PSZ materials depended on the details of the fabrication process. These materials were invariably sintered in the cubic phase field, but then on cooling they passed through the tetragonal-plus-cubic field, in which the tetragonal phase precipitates, and then finally the tetragonal phase undergoes the phase transformation to monoclinic. The evolution of intergranular precipitates discussed by Green et al.,<sup>16</sup> for a Ca-PSZ, and Bansal and Heuer,<sup>17</sup> who were studying a Mg-PSZ, showed that in addition to the intergranular precipitates, there was also a finer dispersion of precipitates within the grains (intragranular). The idea was then put forward that the microstructure could be manipulated by heat treatments in which the precipitation of the tetragonal phase was

controlled.<sup>18</sup> This turned out to be a key philosophy because as we shall see shortly, for particular heat treatments, the tetragonal phase precipitates but does not transform to monoclinic on further cooling. The retention of the high temperature tetragonal phase to room temperature is the key to the fabrication of transformation-toughened materials.

At the same time as the work on thermal shock resistance and microstructural evolution of PSZ was underway, studies were initiated to look at the strength and fracture toughness of these materials. The fracture toughness of a Ca-PSZ was measured by Green et al.<sup>19</sup> and it was found in this particular material that microcracking had occurred during fabrication and though the material had a low strength, it possessed a high fracture surface energy. It was suggested that the propagation of a crack in this material involved the presence of a microcracked process zone at the crack tip and that the energy absorbed in this zone was responsible for the toughness. For a Mg-PSZ, Bansal and Heuer<sup>20</sup> suggested that changes in toughness were a result of the cracks being impeded by the fine dispersion of monoclinic precipitates within the cubic grains.

The discussion in this section has considered materials in which tetragonal (t-)  $ZrO_2$  precipitates and then later transforms to monoclinic (m-)  $ZrO_2$ . It was, however, realized by Claussen<sup>21</sup> that  $ZrO_2$  could also be introduced as a second phase by producing particulate composites. In a study on the mechanical behavior of  $Al_2O_3$ - $ZrO_2$  composites, he found that the  $ZrO_2$  increased fracture toughness and attributed this to stress-induced microcracking. It is interesting to note that a major industry based on the use of fusion cast  $Al_2O_3$ - $ZrO_2$  as an abrasive in grinding wheels had been developed previously and may have indicated that such materials have useful mechanical properties.

The major breakthrough in the mechanical behavior of PSZ came from the work of Garvie et al.,<sup>12</sup> when it was realized that toughening could be produced in materials which contained substantial amounts of the metastable, intragranular tetragonal phase, and that the toughening was associated with the stress-induced transformation of the t- $ZrO_2$  to m- $ZrO_2$ . This process was further elucidated by the work of Porter and Heuer<sup>22</sup> on a Mg-PSZ. To produce the optimum material, the precipitation of the t- $ZrO_2$  must be carefully controlled. This process involves the precipitation of oblate spheroidal, coherent precipitates on the {100} planes of the cubic phase and the aim of the heat treatment is to grow these precipitates to an optimum size. The increase in size changes the degree of metastability. If they are too large ( $\geq 0.1 \mu m$ ), the precipitates transform and this leads to microcracked materials. If they are too small, they are difficult to transform by stress and do not give very much toughening.

As pointed out earlier, these toughening concepts do not apply only to PSZ. There are now a wide range of transformation-toughened particulate composites based on  $ZrO_2$ , such as  $Al_2O_3$ - $ZrO_2$ . Moreover, it was shown by Gupta et al.<sup>23</sup> that in systems such as  $CeO_2$ - $ZrO_2$  and  $Y_2O_3$ - $ZrO_2$ , in which there is a fairly extensive solid solution region, single-phase tetragonal  $ZrO_2$  materials can be produced and that these materials also possessed enhanced strength and toughness. A common feature of all these systems is that the  $ZrO_2$  precipitate or grain size must be kept below a critical size in order to retain the tetragonal phase.

In summary, it was found that the tetragonal phase could be retained metastably at room temperature in many zirconia ceramics, provided the microstructure was carefully controlled. In addition, it was found that the phase transformation could be stress induced and that this led to a considerable increase in fracture toughness of the material. Indeed, fracture toughness values similar to cast iron are now feasible and remarkable strengths of up to 2.5 GPa have been reported. It is the understanding of these concepts and how they can be manipulated that is the primary aim of this book. Since these discoveries, the interest in zirconia has expanded considerably and many of the more recent developments have been discussed in special publications.<sup>24-29</sup>

In addition to the interesting refractory and mechanical properties previously mentioned, there are other properties which make  $ZrO_2$  a particularly fascinating material. For example,

Nerns  
has b-  
electr  
of the  
 $ZrO_2$   
of ox  
electr  
tomot  
electr

The  
refrac  
glaze  
appea  
index  
 $ZrO_2$ ,  
poten  
CSZ.

It i  
forma  
the bc

A. Re  
Cor  
equil  
high t  
that it  
lower  
Figure  
transf  
increa

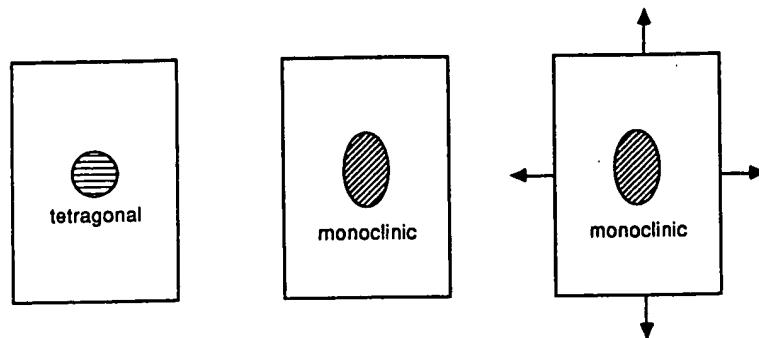


FIGURE 2. A schematic representation of the zirconia phase transformation. The normal phase transformation to monoclinic is represented by going from A to B and indicated that the zirconia particle undergoes a size and shape change. The material surrounding the particle will oppose the transformation and it is the strain energy that is involved in this constraint that allows the tetragonal phase to be retained. As shown in C, the transformation from A to C can be aided by an applied stress.

Nernst<sup>30</sup> used stabilized  $ZrO_2$  as a glower for incandescent lighting and more recently  $ZrO_2$  has been used as high-temperature heating elements, susceptors for induction heating, and electrodes for power generation by magnetohydrodynamics. These applications are a result of the ionic conductivity of  $ZrO_2$ . Wagner<sup>31</sup> established that the defect character of doped  $ZrO_2$  was due to oxygen ion vacancies. Thus, the conductivity of these materials is the result of oxygen ion transport. The ability to conduct oxygen makes  $ZrO_2$  important for many electrochemical applications. Major applications include oxygen sensors for control of automotive emissions, deoxidation of steel, combustion controls for furnaces and engines, electrochemical oxygen pumps, hydrogen production, and high-temperature fuel cells.

The optical properties of CSZ single crystals are also of interest since they possess a high refractive index. Indeed, one of the major uses of  $ZrO_2$  has been as an opacifier for ceramic glazes. It is also possible to grow large single crystals by skull melting.<sup>32</sup> These crystals appear very similar to diamond, especially as a result of the closeness in their refractive indexes. Thus, a flourishing industry for synthetic jewels, based on the production of cubic  $ZrO_2$ , has been established. The ability to grow large crystals of CSZ should lead to other potential uses. For example, tunable laser rods could be produced by appropriately doping CSZ.

#### IV. THE CONCEPT OF TRANSFORMATION TOUGHENING

It is worth reiterating some of the ideas discussed above to give a simple idea of transformation toughening. These ideas will be discussed in greater detail in the remainder of the book but these simple concepts should aid in developing a basis on which to expand.

##### A. Retention of Tetragonal Zirconia

Consider the metal oxide- $ZrO_2$  phase diagram shown in Figure 1. The diagram considers equilibrium conditions and, thus, one expects that the compositions that contain t- $ZrO_2$  at high temperatures will transform to m- $ZrO_2$  upon cooling. It was pointed out earlier, however, that if the t- $ZrO_2$  grain size is less than a critical size, it will remain tetragonal to much lower temperatures. The reason for this metastable retention is depicted schematically in Figure 2. Let us assume that the grain of t- $ZrO_2$  is at a temperature when it is expected to transform to m- $ZrO_2$ . The phase transformation involves a set of transformation strains that increase the volume and change the shape of the particle. If the grain is isolated, the

### H. Transformation of TZP Materials

A complete crystallographic analysis of the tetragonal to monoclinic transformation of TZP materials has not yet been reported. The main studies involving the transformation have described the nucleation and propagation of the monoclinic phase in tetragonal grains.<sup>53,54</sup> It is anticipated, however, that the twin systems would be similar to those observed for other systems where the zirconia particles are confined within a host matrix. The main difference in TZP systems is that the body is composed almost entirely of metastable tetragonal grains. In this situation, when one grain transforms, the accompanying transformation strains are immediately experienced by the adjacent metastable grain, and a situation of "autocatalytic" nucleation of the transformation in the adjacent grain may then follow. This phenomenon has been observed (see, for example, Ruhle et al.<sup>53</sup>).

More recently, evidence has been obtained in a 12 mol % CeO<sub>2</sub>-ZrO<sub>2</sub> TZP alloy that the transformation, occurring around a propagating crack, does not transform the whole grain to the monoclinic form.<sup>55</sup> It appears, therefore, that the deformation around the crack is accommodated by regions (sheets) of monoclinic phase interspersed with regions (blocks) of tetragonal. Hence the toughness is more closely related to a situation of "transformation plasticity" rather than transformation toughening, in that a very small volume fraction of the grain is actually transformed to monoclinic, yet considerable plastic deformation can be accommodated (see also Chapter 4 Section IX).

### V. ALLOY ADDITIVES FOR ZrO<sub>2</sub>

Pure zirconia could not be used for fabricated ceramic forms. Therefore, it has been the custom for at least 50 years to add "stabilizers" to zirconia to retain the high-temperature cubic-fluorite-type phase. Stabilizers found most suitable are aliovalent cubic oxides with cation size ratio differences of <40% that of zirconia, when the coordination number in the lattice is eight, i.e., zirconia in the cubic or tetragonal phase. Table 3 presents some of the common alloying elements and their percentage of ionic radii difference with respect to zirconia.\*

The actual stabilization mechanism is not well understood. In simple terms, stabilization may be brought about by an oxide with a room-temperature-stable cubic structure, causing the distortion of the tetragonal and monoclinic phases back to the cubic form, as suggested by Ryshkewitch.<sup>1</sup> Alternatively, the removal of anions providing a suitable electronic charge balance will allow the cubic structure to survive, as mentioned in Section I. Along similar lines, Barker and Williams<sup>56</sup> have suggested that the nearer the ionic radius of an alervalent stabilization cation is to that of Zr<sup>4+</sup>, the more effective its stabilizing "efficiency" in terms of minimum mole per cent required to yield full stabilization. Thus, Sc<sup>3+</sup> is suggested as the most effective trivalent stabilizer because of the close ionic radii (see Table 3). The reason for its stabilization effectiveness, other authors suggest, is due to the ease of anion ordering while the cation lattice remains disordered, such that the zirconia lattice may adopt a more stable state. The inference here is probably the eightfold coordination of the Zr<sup>4+</sup> which will be adopted on stabilization to tetragonal or cubic symmetry, thereby bringing it closer to a true "ionic" solid.

Traditionally magnesia (MgO), calcia (CaO), and yttria (Y<sub>2</sub>O<sub>3</sub>) have been used as stabilization oxides in commercial materials. Other oxides such as ceria (CeO<sub>2</sub>), scandia (Sc<sub>2</sub>O<sub>3</sub>), lanthanum oxide (La<sub>2</sub>O<sub>3</sub>), and ytterbium oxide (Yb<sub>2</sub>O<sub>3</sub>) are also being used successfully.

By using suitable stabilizer additions, two forms of transformation-toughening zirconia may be produced. These systems may be classified as:

\* The "physical" size that a cation adopts within a host lattice will naturally depend upon the valency it adopts, i.e., the spread of the electron cloud. Therefore, the ionic size shown in Table 3 is merely a rough estimate, as a first approximation, the size ratio correlates very well with this "stabilization" size effect.

**Table 3**  
**IONIC RATIO OF ELEMENTS**  
**OFTEN ALLOYED WITH**  
**ZIRCONIA, SHOWN FOR A**  
**COORDINATION NUMBER OF 8**

Element	Ionic radius (Angstroms)	Difference WRT to $\text{ZrO}_2$
$\text{Zr}^{4+}$	0.84	—
$\text{Ba}^{2+}$	1.42	+69%
$\text{Ca}^{2+}$	1.12	+33%
$\text{Ce}^{4+}$	0.97	+15%
$\text{Hf}^{4+}$	0.83	-1%
$\text{Mg}^{2+}$	0.89	+6%
$\text{Sc}^{3+}$	0.87	+3.6%
$\text{Sr}^{2+}$	1.26	+50%
$\text{Y}^{3+}$	1.019	+21%
$\text{Yb}^{3+}$	1.125	+36%

From Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr.*, A32, 751, 1976. With permission.

1. Precipitated systems, in which the stabilizer has a very low solid solubility in the zirconia lattice, at temperatures where cation migration is still active, i.e.,  $>1400\text{K}$ . Materials produced from such alloying additions are designated PSZ and are derived primarily from additions of  $\text{MgO}$  and  $\text{CaO}$ .
2. Solid solution systems where the stabilizer solubility is such that cation mobility has effectively ceased (or at least slowed down to be commercially practicable) and the stabilizer is retained in solid solution at relatively low temperatures. When formed, such systems are known as TZP and are produced by additions of  $\text{Y}_2\text{O}_3$  and  $\text{CeO}_2$ .

It should also be remembered that two types of phase transformation and reactions are thus possible in zirconia systems, these being diffusional (generally occurring at temperatures  $>1400\text{K}$ ) or diffusionless (military or martensitic, occurring  $<1400\text{K}$ ) as discussed in Section III.

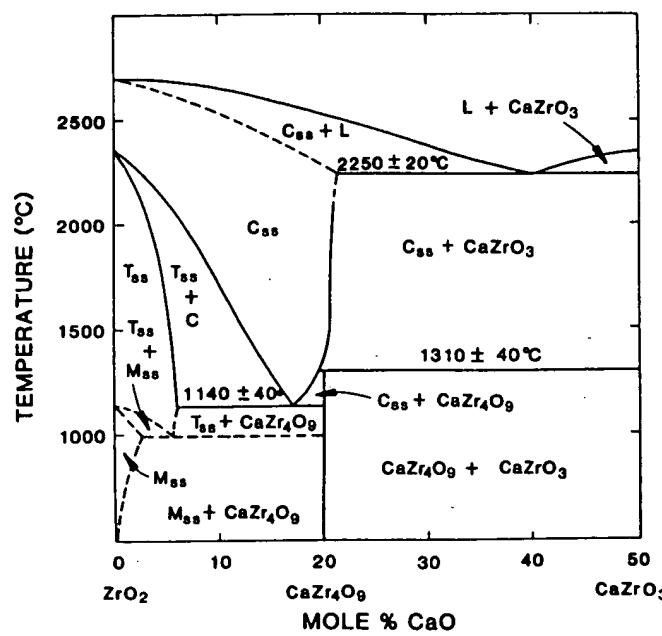
We will briefly examine the binary phase diagrams\* of materials leading to both types of systems. We shall concentrate on those regions of the phase diagrams from which materials, with optimized transformation-toughening properties, may be derived.\*\* While several phase diagrams have generally been proposed for each of the systems described, we shall concentrate only on the diagrams generally found to be the most accurate.

#### A. $\text{CaO-ZrO}_2$

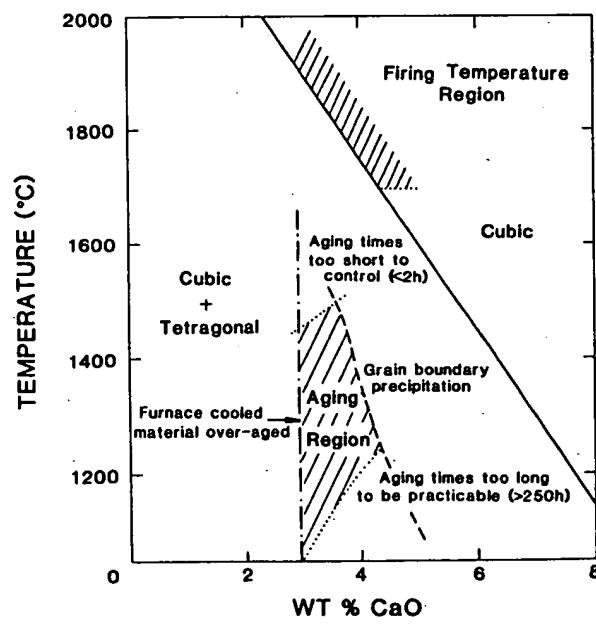
While a number of workers<sup>57-64</sup> have examined the phase relations in the  $\text{CaO-ZrO}_2$  system, confusion concerning the phases present, the actual composition, and the temperature of the eutectoid, still exist. The most recent diagram of the  $\text{ZrO}_2-\text{CaZrO}_3$  region, although also still tentative, is presented Figure 18a. The main confusion in the diagram concerns the

\* The term phase diagram is generally understood to refer to "phase equilibrium diagram." It should be remembered that ZTC materials used for their enhanced mechanical properties are rarely at equilibrium (see Sections IV.B and F).

\*\* While a lot of effort has been expended in determining accurate phase equilibrium diagrams for the various systems (as mentioned in Section IV.A), optimized transformation-toughening materials are *not* at equilibrium.



a



b

FIGURE 18. (a) Proposed equilibrium phase diagram for the  $\text{ZrO}_2\text{-CaO}$  system. (After Stubican, V. S. and Ray, S. P., *J. Am. Ceram. Soc.*, 60, 534, 1977.) (b) "Working" phase diagram for the  $\text{ZrO}_2\text{-CaO}$  system. The solubility of CaO in monoclinic and tetragonal is unknown, but small. (After Hannink, R. H. J., Johnston, K. A., Pascoe, R. T., and Garvie, R. C., *Science and Technology of Zirconia I*, 1981, 116.)

stability of the defect-fluorite  $\phi_1\text{-Ca Zr}_4\text{O}_9$  (20 mol% CaO) and  $\phi_2\text{-Ca}_6\text{Zr}_{19}\text{O}_{44}$  (24 mol% CaO, not shown in phase diagram) phases and the position of the cubic-eutectoid composition at 1140°C and 17 mol% CaO. Hangas et al.<sup>65</sup> have suggested that  $\phi_1$  may be metastable. For practical purposes, the cubic-eutectoid temperature is too low to affect the microstructures of these alloys for engineering applications.

From the diagram, it can be seen that the cubic-fluorite-stabilized-zirconia phase extends from about 10 to 20 mol% CaO at 1700°C. This cubic-stabilized-zirconia (CSZ) phase may be readily retained to room temperature by reasonably fast cooling.\* While CSZ materials find applications as solid electrolytes, their mechanical properties are relatively poor. It was recognized that by lowering the alloy additions, improved materials could be obtained, so that PSZ was produced and a considerable improvement in mechanical properties could be achieved. Prior to 1975, PSZ materials consisted of monoclinic zirconia precipitates dispersed in a CSZ matrix. Present day methods involve cooling the materials sufficiently rapidly from the cubic phase field, suppressing the tetragonal to monoclinic transformation in any precipitates and then bringing these precipitates to a state of metastability as described in Section III.

When fabricating engineering zirconia ceramics for commercial applications, a very limited composition and temperature regime is applicable. Figure 18b shows a typical "working" phase diagram of the CaO-ZrO<sub>2</sub> system.<sup>66</sup> Firing of an 8.4 mol% (4 wt%) CaO-ZrO<sub>2</sub> alloy consists of solution treating at 1800°C, followed by a "rapid" cool and a subsequent reheat to coarsen the previously formed tetragonal precipitates. The method of fabrication of precipitated transformation-toughened zirconia systems is primarily the same for all systems. It is the accurate knowledge of the single phase cubic field and the eutectoid boundaries which are important for successful heat treatment programs in the fabrication process. We shall further discuss the thermal treatment of precipitated zirconia systems later (see Chapter 4).

### B. MgO-ZrO<sub>2</sub>

Diagrams for the MgO-ZrO<sub>2</sub> system have been presented by various workers.<sup>(1,57,67-69)</sup> The phase diagram proposed by Grain<sup>69</sup> has been found to be the most accurate for predicting phase behavior. The zirconia-rich end of the Grain diagram is shown in Figure 19.

At high temperatures, the MgO solubility in ZrO<sub>2</sub> is about 20 mol% at 2000°C, with the cubic phase being stable above 1400°C. At the eutectoid composition, 14 mol% (~5 wt%) MgO, the fully stabilized cubic form is readily retained to room temperature by suitable rapid cooling. Commercial PSZ materials are produced within the composition range 8 to 10 mol% (~2.8 to 3.5 wt%); the reasons for the limited composition range are similar to those depicted in the "working" diagram of the CaO-ZrO<sub>2</sub> system.

The main difference between the CaO-ZrO<sub>2</sub> and MgO-ZrO<sub>2</sub> diagrams is that the eutectoid temperature of the MgO-ZrO<sub>2</sub> system is well known, and occurs at 1400°C. Studies of the decomposition reaction have been performed by various workers. Duwez et al.<sup>57</sup> showed that the cubic solid solution decomposes into MgO and ZrO<sub>2</sub> constituents below 1400°C. Viechnicki and Stubican<sup>68</sup> have examined the decomposition kinetics as a function of MgO content in the range 12 to 20 mol% (~4.3 to 7.5 wt%), i.e., hypereutectoid compositions, and found that the kinetics were not significantly affected by alloy content, but markedly affected by the subeutectoid temperature. These workers observed that the maximum decomposition rate occurred at 1200°C. Farmer et al.<sup>70</sup> examined the kinetics and microstructural relationships of the decomposed products in hypoeutectoid alloys in the range 8 to 11 mol% (~2.8 to 3.9 wt%) MgO. They concluded that the kinetics of the decomposition are

\* It has been found, however, using transmission electron microscopy to examine a radiation/water-quenched 14 mol% CaO-ZrO<sub>2</sub> sample from 2000°C, that the formation of very small tetragonal precipitates within the CSZ matrix could not be suppressed.<sup>106</sup>

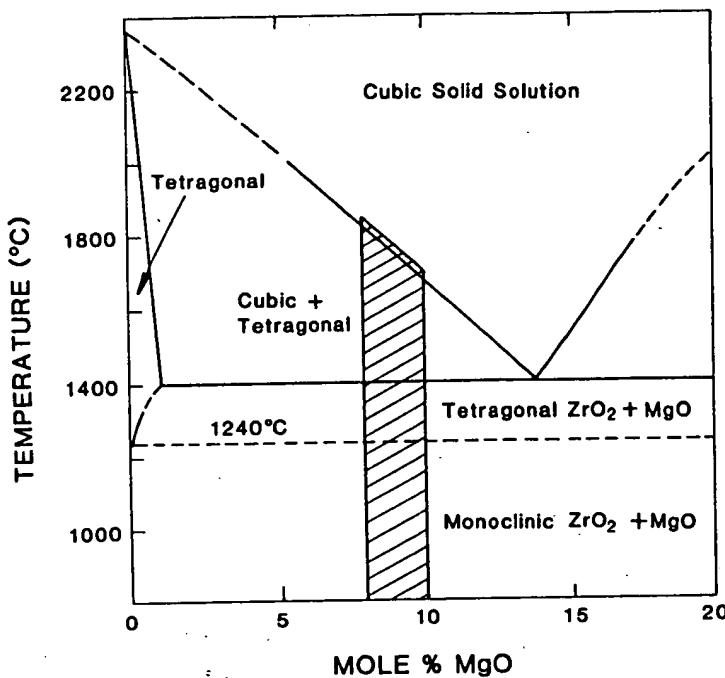


FIGURE 19. Zirconia-rich end of the MgO-ZrO<sub>2</sub> phase equilibrium diagram.  
(After Grain, C. F., *J. Am. Ceram. Soc.*, 50, 288, 1967.)

nucleation controlled, and microstructures produced may be categorized as a cellular reaction composed of rods growing perpendicular to the advancing reaction front.

All the investigations of the decomposition reaction agree with the predictions of the phase diagram (Figure 19), namely:

1.  $\geq 1200^\circ\text{C}$  Mg-CSZ  $\rightarrow$  tetragonal ZrO<sub>2</sub> + MgO, on cooling tetragonal ZrO<sub>2</sub>  $\rightarrow$  monoclinic ZrO<sub>2</sub>
2.  $\leq 1200^\circ\text{C}$  Mg-CSZ  $\rightarrow$  monoclinic ZrO<sub>2</sub> + MgO

An ordered compound, Mg<sub>2</sub>Zr<sub>5</sub>O<sub>12</sub> (not included in the phase diagram), was reported by Delamarre<sup>71</sup> to exist in stable equilibrium above 1800°C. In association with the decomposition reaction, the compound Mg<sub>2</sub>Zr<sub>5</sub>O<sub>12</sub> occurs as a metastable precursor to the decomposition reaction.<sup>20,72-75</sup> Hannink<sup>72</sup> has observed the occurrence of the compound in eutectoid and hypoeutectoid compositions as micro domains. These domains are stable  $< 1400^\circ\text{C}$  and may be induced in the range 1000 to 1300°C, after a suitable nucleation step  $< 800^\circ\text{C}$ . The Mg<sub>2</sub>Zr<sub>5</sub>O<sub>12</sub> prefers to nucleate and grow at the CSZ matrix-ZrO<sub>2</sub> precipitate interface, and is stable until the grain itself is consumed by the decomposition reaction. The effect of this phase on the mechanical properties is further discussed in Chapter 4.

A problem still exists in the phase diagram in that the precise solubility of MgO in monoclinic and tetragonal zirconia is not known with certainty. This arises because the spatial resolution of the instruments used to measure the MgO contents are not sufficiently accurate to determine MgO levels at low concentrations.

### C. Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>

This system has been extensively studied.<sup>76-83</sup> The main disagreements among all the diagrams is that of the eutectoid temperature. It is generally accepted, as a result of subsequent

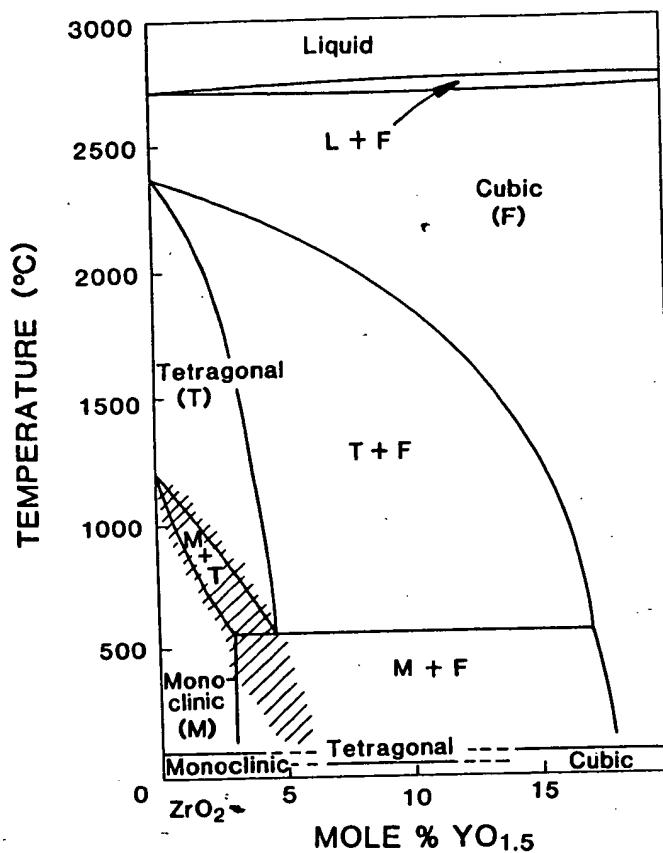


FIGURE 20. Zirconia-rich end of the yttria-zirconia phase equilibrium diagram. Nonequilibrium homogeneous phases are indicated at the lower margin. Hatched region indicates nonequilibrium monoclinic-tetragonal transition. (After Scott, H. G., *J. Mater. Sci.*, 10, 1527, 1975.)

work, that the diagram of Scott<sup>81</sup> is the most accurate for ceramic processing purposes. The zirconia-rich end of Scott's diagram is shown in Figure 20. For fabrication purposes, the zirconia-rich end at temperatures above 1300°C is of most importance.

There are two essential differences between this system and the previously described  $\text{CaO}-\text{ZrO}_2$  and  $\text{MgO}-\text{ZrO}_2$  diagrams in terms of transformation-toughening zirconia ceramics. First, the extent of the tetragonal solid solution range is much larger in the yttria-based system, and second, the temperature of the tetragonal to monoclinic transformation is very low. The hatched region in Figure 20 indicates the nonequilibrium monoclinic transition.

Commercial transformation-toughening ceramics are generally produced within the composition range 2.5 to 3.5 mol % (~3 to 6 wt %)  $\text{Y}_2\text{O}_3-\text{ZrO}_2$ , by firing at 1400 to 1500°C followed by rapid cooling. This thermal treatment method forms the class of zirconia ceramics known as TZP. Precipitated PSZ materials can also be produced from composition in the range 3 to 6 mol % (~5 to 10 wt %)  $\text{Y}_2\text{O}_3-\text{ZrO}_2$ .

Because of the importance of the subsolidus (t)/(t-c) and (t-c)/(c) boundaries in the fabrication of commercial ceramics, Ruhle et al.<sup>53</sup> and Lanteri et al.<sup>84</sup> have independently attempted to determine the precise location of these boundaries. Their results, in relation to those of Scott,<sup>81</sup> are shown in Figure 21. The discrepancy is not large and has been accounted for in terms of the Cahn and Larche<sup>85</sup> model for coherent phase equilibrium.

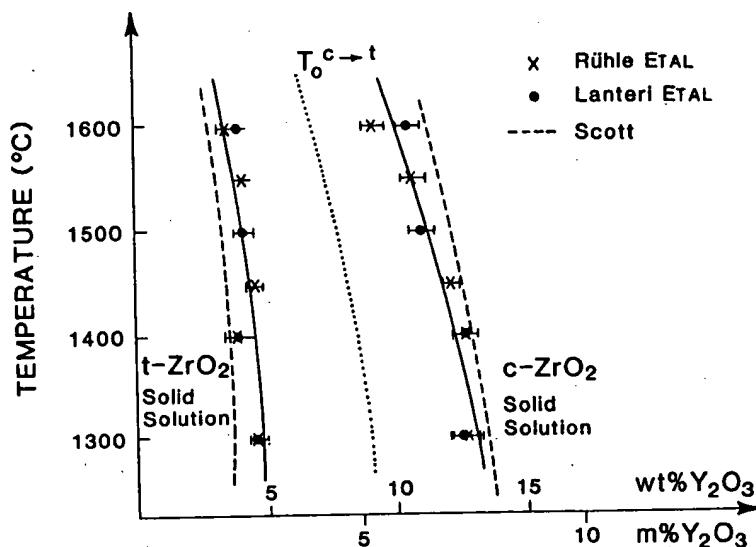


FIGURE 21. Zirconia-rich end of the yttria-zirconia phase equilibrium diagram. The equilibrium compositions were determined by energy dispersive X-ray spectroscopy. (Reference data from Ruhle et al.,<sup>53</sup> Lenteri et al.,<sup>54</sup> and Scott.<sup>81</sup> (After Ruhle, M., Claussen, N., and Heuer, A. H., *Science and Technology of Zirconia II*, 1984, 352.)

#### D. CeO<sub>2</sub>-ZrO<sub>2</sub>

The CeO<sub>2</sub>-ZrO<sub>2</sub> system is another alloy system which shows considerable industrial potential. The zirconia-rich end of the Duwez and Odell<sup>86</sup> CeO<sub>2</sub>-ZrO<sub>2</sub> phase diagram is shown in Figure 22. This system, like the yttria-zirconia system, also has an extensive solid-solution tetragonal phase field and has the monoclinic transformation temperature of a 20 mol% CeO<sub>2</sub>-ZrO<sub>2</sub> alloy at about room temperature.

While modification concerning a eutectoid at 270°C has been proposed by Lange,<sup>87</sup> the phase field at the temperatures required for fabrication purpose, ~1400 to 1600°C, has not been disputed.

## VI. RETENTION OF TETRAGONAL ZIRCONIA

Retention of the tetragonal phase is the most important factor for the utilization of the transformation-toughening phenomenon. As we have seen, under normal conditions of temperature and pressure, large particles of constrained pure tetragonal zirconia commence to transform to the monoclinic form at about 1200°C, the M<sub>s</sub> temperature. Transformation continues over a temperature range of about 100°C until it is finished at the M<sub>f</sub> temperature. We have seen in Sections IV.E and V that the M<sub>s</sub> temperature may be reduced, i.e., the tetragonal phase is retained by a number of mechanisms comprised essentially of chemical and physical effects.

Tetragonal particle/grain size retention (stability) has been addressed by a number of authors<sup>37,87-93</sup> using a number of approaches. As shown in Section IV.E, the stability of the tetragonal phase is most readily described in terms of the thermodynamics of the transformation. This approach determines the total free energy change associated with the transformation, of a spherical particle, by considering variables such as bulk and surface energy terms. We shall briefly review the retention of the tetragonal form for various conditions and situations of the zirconia particles. In this approach, we neglect the nucleation conditions

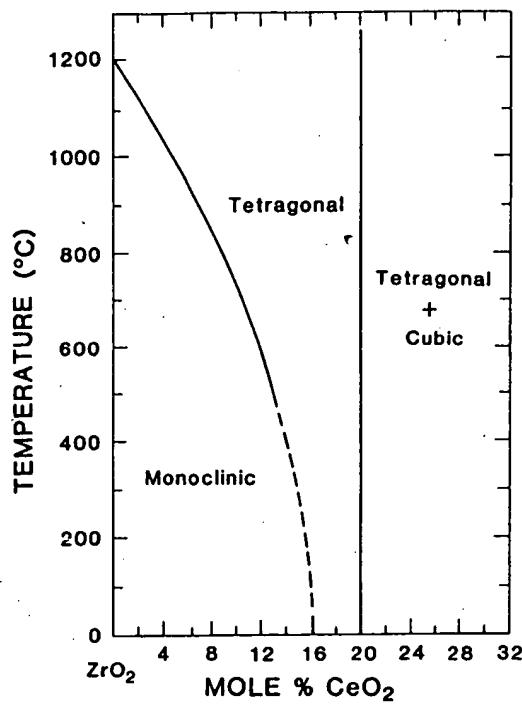


FIGURE 22. Zirconia-rich end of the  $\text{ZrO}_2\text{-CeO}_2$  phase equilibrium diagram. (After Duwez, P. and Odell, P., *J. Am. Ceram. Soc.*, 33, 274, 1950.)

(see Section IV.E) in order to give a simple explanation of the critical size effect associated with retention of t-ZrO<sub>2</sub>.

#### A. Unconstrained Particles

Very small "unconstrained" particles of tetragonal zirconia are known to exist in the free state at room temperature. The small particle-size effect has been considered by Garvie<sup>88</sup> using end-point-thermodynamic calculations. This approach yields the free energy, F, of a particle as

$$F = (4/3)\pi r^3 F_{\text{chem}} + 4\pi r^2 S_{\text{chem}} \quad (2)$$

where  $F_{\text{chem}}$  is the free energy/unit volume of a large crystal; r, the radius of a crystal under consideration; and  $S_{\text{chem}}$ , surface energy of the crystal.

The difference in free energy between the tetragonal and monoclinic polymorphs is then given by:

$$\Delta F_0 = (4/3)\pi r^3 (F_T - F_M) + 4\pi r^2 (S_T - S_M) \quad (3)$$

where the subscripts T and M refer to the tetragonal and monoclinic polymorphs, respectively. The tetragonal form can exist by considering a critical value of  $r_c$  when  $\Delta F_0$  is zero at a particular temperature below the normal transformation temperature. Thus, we can write:

$$r_c = -3(F_T - F_M)/(S_T - S_M) \quad (4)$$

Therefore, at or below some critical particle size, the bulk and surface energy balance

# SOLIDUS SURFACE AND PHASE EQUILIBRIA DURING THE SOLIDIFICATION OF ALLOYS IN THE $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$ SYSTEM



S. N. Lakiza, L. M. Lopato,  
and V. P. Smirnov

UDC 546.31:621:641:831

The projection of the solidus surface in the  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  phase equilibrium diagram was plotted. The scheme of alloy solidification indicates that the primarily congruent modes of phase transformation in the limiting binary systems are retained in the ternary system.

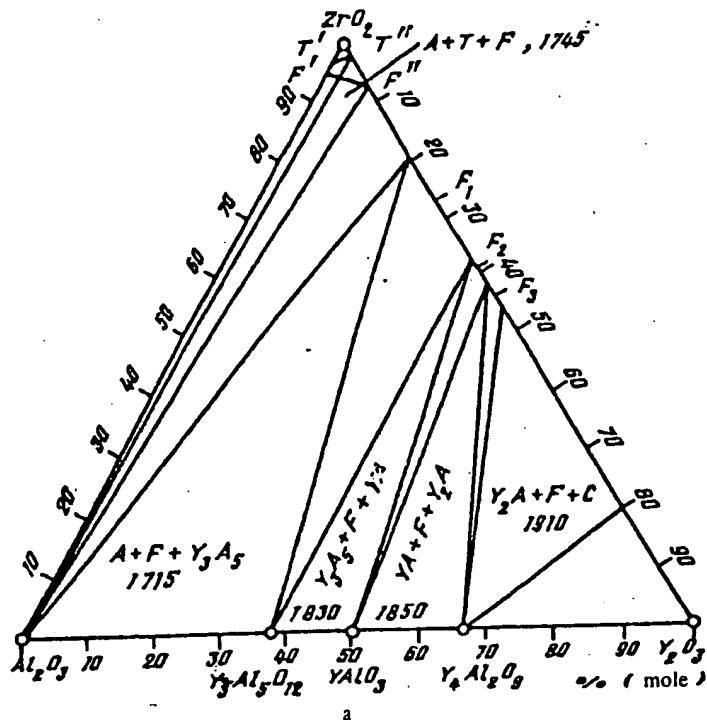
The structure of the limiting binary systems [1-14], phase triangulation [15], liquidus surface [16], and isothermal sections at 1250, 1450, 1600, 1650, and 1800°C [17-20] are known for the  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  system. Authors of the isothermal section at 1800°C [18] maintain that all phases of the system are in the solid state at that temperature. However, a ternary eutectic has been found at  $1715 \pm 20^\circ\text{C}$  [16] including the phases  $\text{Al}_2\text{O}_3(\text{A}) + \text{F} + \text{Y}_3\text{Al}_5\text{O}_{12}(\text{Y}_3\text{A}_5)$ , where F is a  $\text{ZrO}_2$ -based solid solution with the fluorite structure containing various amounts of  $\text{Y}_2\text{O}_3$ . A proposed variant of the isothermal section [18] should be directed at least to this temperature.

The objective of the present work was to construct a projection of the solidus surface on the concentration triangle, and study the solidification processes in  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  alloys.

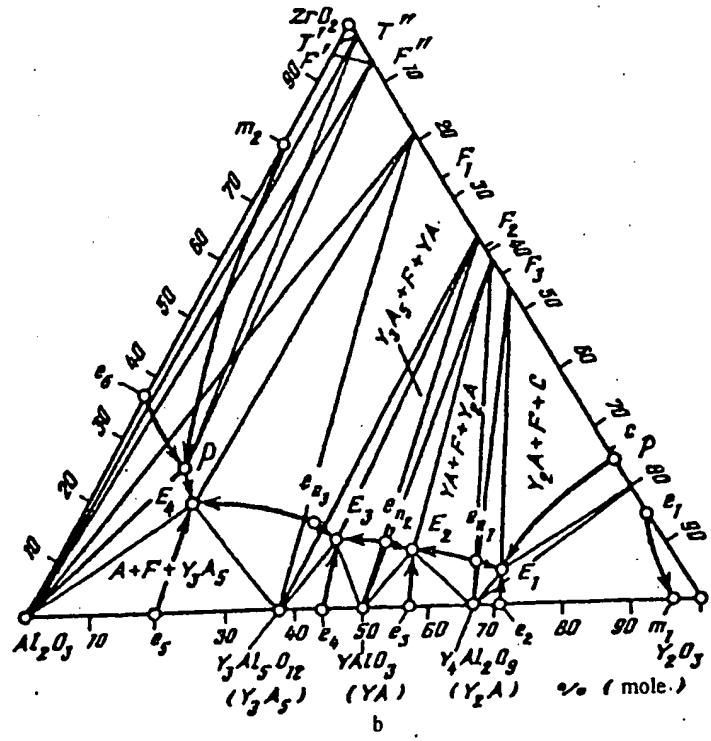
TABLE I. Phase Compositions and Initial Melting Temperatures of Specimens in the 50  $\text{Al}_2\text{O}_3$ -50  $\text{ZrO}_2-\text{Y}_2\text{O}_3$  Section, Indicating the Location of Phase Fields on the Solidus Surface of the  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  Phase Equilibrium Diagram

$\text{Al}_2\text{O}_3$	Composition, mole %		Phase composition	Solidus Temperature, °C
	$\text{ZrO}_3$	$\text{Y}_2\text{O}_3$		
48,5	48,5	3,0	A+T+E	1750
47,5	47,5	5,0	A+T	1745
45,0	45,0	10,0	A+F	1730
42,5	42,5	15,0	A+F+Y <sub>3</sub> A <sub>5</sub>	1715
40,0	40,0	20,0	The same	1710
37,5	37,5	25,0	" "	1715
35,0	35,0	30,0	Y <sub>3</sub> A <sub>5</sub> +F	1740
33,5	35,5	33,0	The same	1865
32,5	32,5	35,0	" "	1845
30,0	30,0	40,0	Y <sub>3</sub> A <sub>5</sub> +F+YA	1840
27,5	27,5	45,0	YA+F	1870
25,0	25,0	50,0	YA+F+Y <sub>3</sub> A	1860
22,5	22,5	55,0	The same	1850
21,0	21,0	58,0	Y <sub>3</sub> A+F	1940
20,0	20,0	60,0	Y <sub>3</sub> A+F+C	1915
17,5	17,5	65,0	The same	1905
15,0	15,0	70,0	" "	1910
12,5	12,5	75,0	Y <sub>3</sub> A+C	1915
10,0	10,0	80,0	The same	1925
7,5	7,5	85,0	" "	1925
5,0	5,0	90,0	" "	1935
2,5	2,5	95,0	" "	1950

Institute of Materials Science Problems, Ukrainian Academy of Sciences, Kiev. Translated from Poroshkovaya Metallurgiya. Nos. 1/2(377), pp. 71-76, January-February, 1975. Original article submitted September 13, 1993.



a



b

Fig. 1. Projection of the solidus surface (a) and the equilibrium solidification diagram for alloys (b) of the  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  system.

TABLE 2. Coordinates of the Apices of the Conodal Triangles for the Solid Phases on the Solidus Surface of the  $\text{Al}_2\text{O}_3$ — $\text{ZrO}_2$ — $\text{Y}_2\text{O}_3$  System, According to Data Obtained by Microprobe Analysis

Phase field	Compositions of the equilibrium phases, mole %					
	$\text{Al}_2\text{O}_3$	$\text{Y}_2\text{A}_3$	F	YA	$\text{Y}_2\text{A}$	C
$\text{A}+\text{F}+\text{Y}_2\text{A}_3$	0,1/0,06*	0,5/37,4	80,8/19,2			
$\text{Y}_2\text{A}_3+\text{F}+\text{YA}$		1,4/40,5	60,7/39,3	0,80/50,4		
$\text{YA}+\text{F}+\text{Y}_2\text{A}$			59,2/40,8	0,03/50,2	1,0/67,3	
$\text{Y}_2\text{A}+\text{F}+\text{C}$			44,0/56,0		0,3/67,7	19,1/80,9

\*The concentration of  $\text{ZrO}_2$  is given before, and of  $\text{Y}_2\text{O}_3$  after the slash.

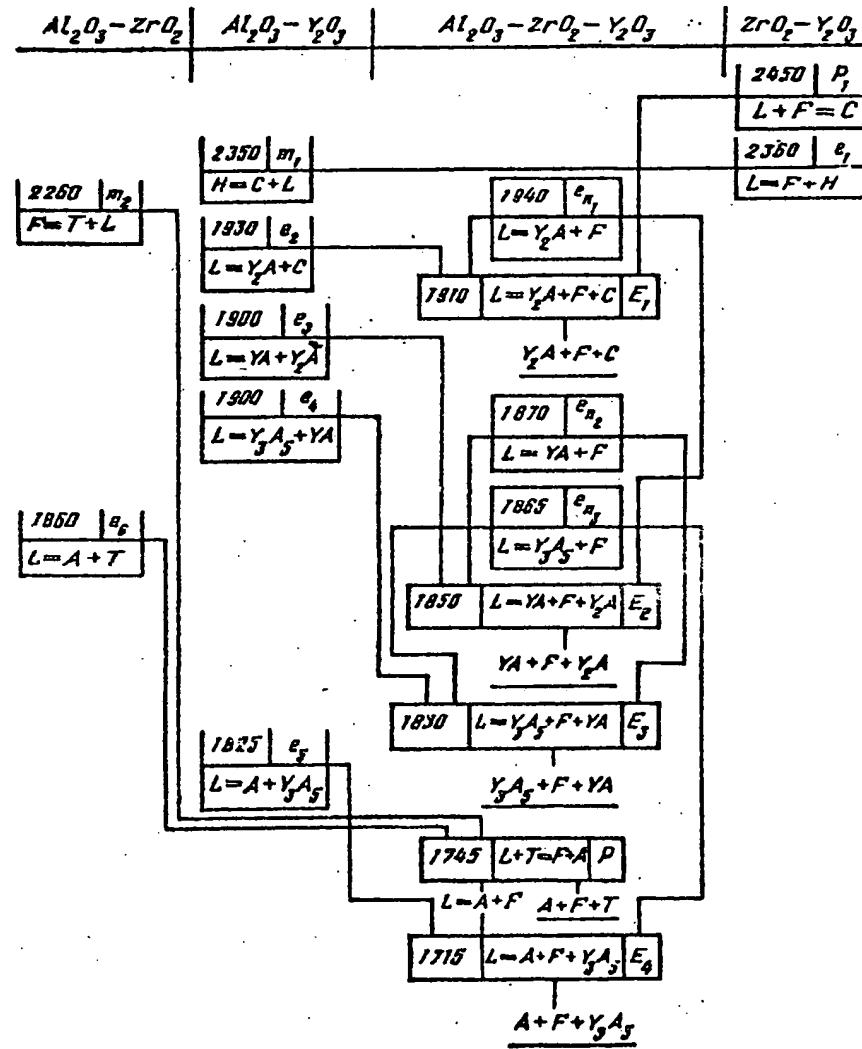


Fig. 2. Reaction scheme for the equilibrium solidification of specimens in the  $\text{Al}_2\text{O}_3$ — $\text{ZrO}_2$ — $\text{Y}_2\text{O}_3$  system.

The starting materials, and methods of preparing and studying the specimens, are described in [15, 16]. Coordinates of the apices of the conodal triangles were determined by microprobe analysis using the "Kamebaks SX-50" unit of the firm "Kameka" (France).

The results of the investigation are shown Fig. 1 in the form of a projection of the solidus surface on the concentration triangle (a), and a solidification diagram (b), for the system. The beginning melting temperatures and phase compositions of alloys in the 50 mole %  $\text{Al}_2\text{O}_3$ -50 mole %  $\text{ZrO}_2-\text{Y}_2\text{O}_3$  section, characterizing the positions of the phase fields on the solidus surface, are given in Table 1.

No ternary compounds or ternary solid solution fields are observed in the  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  system. The solidus surface consists of five isothermal three-phase fields corresponding to four invariant equilibria of the eutectic type and one of the peritectic type, ruled surfaces representing the end of solidification of the binary eutectics  $A + T$ ,  $A + F$ , and  $\text{Y}_4\text{Al}_2\text{O}_9(\text{Y}_2\text{A}) + C$  (where  $T = \text{solid solution based on tetragonal } \text{ZrO}_2$  containing various amounts of  $\text{Y}_2\text{O}_3$  and  $C = \text{solid solution based on } \text{C}-\text{Y}_2\text{O}_3$  containing various amounts of  $\text{ZrO}_2$ ), and the ruled surface  $F'T'T''F''$  formed by the sides of the conodal triangles based on the equilibrium phases  $T$  and  $F$ , whose compositions lie close to the  $\text{ZrO}_2$  corner and vary along the curves  $T'T''$  and  $F'F''$  (Fig. 1a). Data on the coordinates of the conodal triangles are given in Table 2. The microprobe data are confirmed by the results of x-ray diffraction analysis [15].

Between the liquidus and solidus surfaces, the ternary equilibrium diagram contains volumes in which solidification of the binary eutectics  $A + T$ ,  $A + F$ ,  $A + \text{Y}_3\text{A}_5$ ,  $\text{Y}_3\text{A}_5 + F$ ,  $\text{Y}_3\text{A}_5 + A$ ,  $YA + F$ ,  $YA + \text{Y}_2\text{A}$ ,  $\text{Y}_2\text{A} + F$ , and  $\text{Y}_2\text{A} + C$  occurs. These are included within the corresponding ruled surfaces and isothermal planes of the invariant transformations.

Figure 2 shows the scheme of reactions for the equilibrium solidification of specimens in the  $\text{Al}_2\text{O}_3-\text{ZrO}_2-\text{Y}_2\text{O}_3$  system. Equilibrium solidification of the alloys is basically characterized by four invariant transformations at 1910 ( $E_1$ ), 1850 ( $E_2$ ), 1830 ( $E_3$ ), and 1750°C ( $E_4$ ). A transition from the incongruent three-phase transformation  $L_p + F = C$  to the congruent transformation  $L = F + C$  occurs along the monovariant curve  $pE_1$ . This is terminated by the four-phase invariant transformation  $L_{E_1} = \text{Y}_2\text{A} + F + C$ . A three-phase equilibrium characteristic of a metatetic process  $F = T + L$  occurs along the limiting curve  $m_2P$  as the temperature decreases from 2260 to 1745°C, and is followed by the four-phase invariant equilibrium  $L_p + T = F + A$  at this temperature. The monovariant process  $L = F + A$ , which takes place immediately after the peritectic reaction  $P$ , occurs with decreasing temperature along the limiting curve  $PE_4$  and is congruent in nature. The point  $E_4$  corresponds to the composition of the liquid which participates in the four-phase invariant equilibrium  $L_{E_4} = A + F + \text{Y}_3\text{F}_5$  (1715°C). Two additional three-phase congruent processes are terminated at this point:  $L = A + \text{Y}_3\text{A}_5$ , and  $L = \text{Y}_3\text{A}_5 + F$ .

## REFERENCES

1. F. Schmid and D. Viechnicki, "Oriented eutectic microstructures in the  $\text{Al}_2\text{O}_3-\text{ZrO}_2$  system," *J. Mater. Sci.*, **5**, No. 6, 470-473 (1970).
2. G. R. Fischer, L. J. Manfredo, R. N. McNally, et al., "The eutectic and liquidus in the  $\text{Al}_2\text{O}_3-\text{ZrO}_2$  system," *J. Mater. Sci.*, **16**, No. 12, 3447-3451 (1981).
3. J. Echigoya, Y. Takabayashi, K. Sasaki, et al., "Solidification microstructure of  $\text{Y}_2\text{O}_3$ -added  $\text{Al}_2\text{O}_3-\text{ZrO}_2$  eutectic," *Trans. Jpn. Inst. Metals*, **27**, No. 2, 102-107 (1986).
4. A. V. Shevchenko, L. M. Lopato, G. I. Gerasimuk, et al., "The  $\text{HfO}_2-\text{ZrO}_2-\text{Al}_2\text{O}_3$  system," *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, **26**, No. 4, 839-842 (1990).
5. V. S. Stubican, R. J. Hink, and S. P. Ray, "Phase equilibrium and ordering in the system  $\text{ZrO}_2-\text{Y}_2\text{O}_3$ ," *J. Am. Cer. Soc.*, **61**, No. 1/2, 17-21 (1978).
6. A. V. Shevchenko, V. D. Tkachenko, L. M. Lopato, et al., "Method for determining phase transformation temperatures with the use of solar heating," *Poroshk. Metall.*, No. 1, 91-95 (1986).
7. A. V. Shevchenko, L. M. Lopato, T. V. Obolonchik, et al., "Liquidus surface of the  $\text{HfO}_2-\text{ZrO}_2-\text{Y}_2\text{O}_3$  system," *Izv. Akad. Nauk. SSSR, Neorg. Mater.*, **23**, No. 3, 452-456 (1987).
8. N. A. Toropov, I. A. Bondar', F. Ya. Galakhov, et al., "Phase equilibria in the yttrium oxide-alumina system," *Izv. Akad. Nauk. SSSR, Ser. Khim.*, No. 7, 1158-1164 (1964).
9. D. Viechnicki and F. Schmid, "Investigation of the eutectic point in the system  $\text{Al}_2\text{O}_3-\text{Y}_3\text{Al}_5\text{O}_{12}$ ," *Mater. Res. Bull.*, **4**, No. 2, 129-135 (1969).
10. J. L. Caslavski and D. J. Viechnicki, "Melting behavior and metastability of yttrium aluminum garnet (YAG) and  $\text{YAlO}_3$  determined by optical differential thermal analysis," *J. Mater. Sci.*, **15**, No. 7, 1709-1718 (1980).

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**